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(54) COATING COMPOSITION FOR IMPROVING PERFORMANCE OF LITHOGRAPHY AND PATTERN FORMING METHOD USING THE COATING COMPOSITION**(57)Abstract:**

PURPOSE: To provide a coating compsn. for improving performances of lithography and to provide a pattern forming method using the coating compsn.

CONSTITUTION: This coating compsn. is an alkali compsn. to be applied on the upper surface of a quinonediazide photoresist compsn. coating film. The coating compsn. is applied on the upper surface of a quinonediazide photoresist compsn. coating film formed on a substrate, irradiated with light to transfer a latent image of a pattern, then heat-treated and developed. Thereby, only by coating one kind of surface coating compsn., a good pattern can easily be formed having resolution, good shape and focal depth of the transferred pattern and little changes in the dimension of the transferred pattern without depending on the coating film thickness.

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CLAIMS

[Claim(s)]

[Claim 1] The application constituent for the improvement in a performance in lithography which is an application constituent used applying to the upper surface of a quinone diazide system photoresist constituent application film, and is characterized by the alkaline thing.

[Claim 2] A water-soluble application constituent according to claim 1.

[Claim 3] The application constituent containing a photosensitive acid generating compound according to claim 1 or 2.

[Claim 4] An application constituent given in any of the claims 1-3 containing a fluorine compound they are.

[Claim 5] An application constituent given in any of the claims 1-4 containing the compound to which the absorbance to the wavelength of the incident light of an application constituent application film decreases by projection of the incident light concerned they are.

[Claim 6] The pattern formation method characterized by developing negatives after applying an application constituent given in any of claims 1-5 they are to the upper surface of the quinone diazide system photoresist constituent application film applied on the substrate, projecting light, imprinting a pattern latent image and heat-treating subsequently.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the pattern formation method which used the application constituent for the improvement in a performance in lithography, and the application constituent concerned.

[0002]

[Description of the Prior Art] In recent years, the process tolerance of ultra-fine processing technology (photo lithography technology) used for manufacture of an integrated circuit etc. is improving remarkably, for example, submicron processing technology is established as technology of mass-production-method level in a dynamic random access memory (DRAM). As the exposure light source, for submicron processing, the light of short wavelength, such as g line (436nm), i line (365nm), and KrF excimer laser light (248nm), is used, and various highly efficient photoresist application constituents are proposed as a photoresist constituent used.

[0003] As a property required of the above-mentioned photoresist application constituent (the pattern formation method), the highly efficient photoresist application constituent (the pattern formation method) equipped with properties, like that near of the configuration of an imprint pattern is more good to rectangle nature and the depth of focus is large is called for as well as being a high definition more. For this purpose achievement, beforehand, after carrying out the alkali treatment of the photoresist application constituent, photofading nature material is applied on the method of performing a pattern imprint, or a photoresist constituent application film, and the method of raising the contrast of the incident light on efficiency etc. is proposed (12 vol Semicon NEWS, 8, 60 (1988)).

[0004] Moreover, in order to lessen more size change of the imprinted pattern by application thickness, The light which is made to form a transparent film with a different refractive index from it, and is reflected from the photoresist constituent application film upper surface on a photoresist constituent application film, Pass through this photoresist constituent application film upper surface, and interference of phase contrast with the light reflected from the film upper surface where the newly applied refractive indexes differ is used. The method of making small influence of the above-mentioned multiple echo in a film, and raising a size controllability is proposed (JP,60-149130,A, JP,62-62520,A, JP,62-62521,A, JP,5-188598,A, etc.).

[0005] However, since the alkali treatment of the whole surface surface of an application film is carried out, originally, the alkali treatment of the case of the method by the alkali treatment of an application film is carried out to the exposure portion which does not need an alkali treatment, consequently it has the problem said that *****, such as scum, occur. Moreover, the present condition is that the method of improving a pattern configuration is not proposed at the same time in the case of the method of using the application film of a low refractive index only a constituent still acid as a constituent which attains a low refractive index (1.45 or less) with a meaning on a process is known, therefore it makes size change of a pattern small.

[0006]

[Problem(s) to be Solved by the Invention] this invention is made in view of the above-mentioned actual condition, and the purpose is in offering the pattern formation method of the configuration and the depth of focus of an imprint pattern being good, and change by the application thickness of an imprint pattern size being small, and giving a good result, by high resolving by the easy method of applying one kind of surface application constituent.

[0007]

[Means for Solving the Problem] Namely, the 1st summary of this invention is an application constituent used applying to the upper surface of a quinone diazide system photoresist constituent application film. It consists in the application constituent for the improvement in a performance in lithography characterized by the alkaline thing, the 2nd summary The above-mentioned application constituent is applied to the upper surface of the quinone diazide system photoresist constituent application film applied on the substrate, light is projected, a pattern latent image is imprinted, and it consists in the pattern formation method characterized by subsequently developing negatives after heat-treating.

[0008] Hereafter, this invention is explained in detail. Although this invention is applicable to the both sides of the conventionally well-known negative mold and positive type which consist of a quinone diazide system photoresist application constituent, it is suitable for a positive-type photoresist application constituent especially. Generally the photoresist application constituent of a quinone diazide system positive type contains an alkali fusibility resin, a quinone diazide compound, and a solvent. As an alkali fusibility resin, although a novolak resin, polyhydroxy styrene or its derivative, a styrene maleic anhydride copolymer, etc. are mentioned, a novolak resin, polyhydroxy styrene, or its derivative is suitable. A

novolak resin can carry out the heating polycondensation of a hydroxy aromatic compound and the carbonyl compound under existence of an acid catalyst, and can obtain them.

[0009] As the above-mentioned hydroxy aromatic compound, for example A phenol, o-cresol, m-cresol, p-cresol, 3-ethylphenol, 2, 5-xyleneol, The phenols; 2-methoxy phenol which may be replaced by an alkyl group or aryl groups, such as 3, 5-xyleneol, and a phenylphenol Alkoxy **, such as 4-methoxy phenol and 4-phenoxy phenol, an allyloxy phenols; alpha naphthol, The naphthols which may be replaced by alkyl groups, such as a beta naphthol and a 3-methyl-alpha naphthol; 1, 3-dihydroxybenzene, The polyhydroxy benzens which may be replaced by alkyl groups, such as a 1, 3-dihydroxy-2-methylbenzene, 1 and 2, 3-trihydroxy benzene, 1 and 3, 5-trihydroxy benzene, 1 and 2, and 3-trihydroxy-5-methylbenzene, are mentioned.

[0010] as the above-mentioned carbonyl compound, a formaldehyde, a paraformaldehyde, an acetaldehyde, etc. are aliphatic, for example -- alkyl ketones [, such as an aromatic-aldehydes; acetone,], such as an aldehydes; benzaldehyde and a hydroxy benzaldehyde, are mentioned As the above-mentioned acid catalyst, a hydrochloric acid, a sulfuric acid, oxalic acid, etc. are mentioned, for example.

[0011] As polyhydroxy styrene, polymerization objects, such as 4-hydroxystyrene, 3-methyl-4-hydroxystyrene, and 3-chloro-4-hydroxystyrene, are mentioned, for example. As a polyhydroxy styrene derivative, the copolymer of the above-mentioned polyhydroxy styrene and other components is mentioned, and acrylic-acid derivatives, such as maleic-acid derivative; acrylic acids, such as ethylene derivative; maleic acids, such as styrene derivative; ethylene, such as styrene, 4-methyl styrene, and a stilbene, and a propylene, 2-methyl maleic acid, and N-(4-hydroxyphenyl) maleimide, a methacrylic acid, an ethyl acrylate, and an ethyl methacrylate, etc. are mentioned as other components.

[0012] In order that the above-mentioned novolak resin, polyhydroxy styrene, or its derivative may make the extinction of a short wavelength field low if needed, it may be returned by hydrogen etc., and you may have the bad influence in this invention, and may have substituents, such as a halogen atom, a nitro group, and an ester machine, in the limitation [give] and the ring. Moreover, some hydroxyl groups of phenol nature may be replaced as etherification objects, such as esterification object; methyl ethers, such as t-butyloxy carbonate and acetate, the trimethylsilyl ether, and the tetrahydropyranyl ether.

[0013] the optimal weight average molecular weight of an alkali fusibility resin -- usually -- 2000-30000 -- it is 3000-20000 preferably Moreover, the resin except the low molecular weight constituent in the above-mentioned resin or the resin which made molecular weight distribution large by mixing two or more kinds of resins from which molecular weight differs can also be used in fractional precipitation etc.

[0014] As a quinone diazide compound, usually 1, a 2-benzoquinone diazido-4-sulfonic acid, Orthoquinone diazido compounds, such as ester, such as a 1, 2-naphthoquinonediazide-4-sulfonic-acid, 1, and 2-naphthoquinonediazide-5-sulfonic acid, or an amide, are mentioned. Specifically Polyhydroxy alkyl compounds, such as a glycerol and a pentaerythritol, A novolak resin, bisphenol A, 4, 4', a 4"-trihydroxy phenylmethane; Polyhydroxy aromatic compounds, such as a gallate, a quercetin, a morin, and a polyhydroxy benzophenone, and 1, a 2-benzoquinone diazido-4-sulfonic acid, Ester, such as a 1, 2-naphthoquinonediazide-4-sulfonic-acid, 1, and 2-naphthoquinonediazide-5-full phon acid, is mentioned. Especially in these, the ester of a phenolic compound is desirable. Moreover, the sensitization agent which usually contains two or more orthoquinone diazido machines [three or more] preferably in 1 molecule is desirable.

[0015] As a solvent, carboxylates; ethylene glycol methyl ethers, such as ethyl acetate, butyl acetate, and gamma-butyrolactone, Ethylene glycol ethyl ether, a propylene-glycol methyl ether, Propylene-glycol ethyl ether, a diethylene-glycol wood ether, Glycol ethers, such as a dipropylene-glycol wood ether; Ethylene glycol ethyl ether acetate, Glycol-ether alkyl carboxylates, such as propylene-glycol methyl-ether acetate and propylene-glycol methyl-ether propionate; A methyl lactate, Hydroxyalkyl carboxylates, such as an ethyl lactate; 3-methoxy methyl propionate, A 3-ethoxy methyl propionate, a 3-ethoxy ethyl propionate, Alkoxy alkyl carboxylates, such as a 2-methyl-3-methoxy methyl-propionate and 2-methyl-3-ethoxy ethyl propionate; A pyruvic-acid methyl, Pyruvic-acid ester, such as pyruvic-acid ethyl; independent or two or more kinds of mixed solvents, such as ketones, such as a methyl ethyl ketone, a methyl amyl ketone, and a cyclohexanone, are mentioned.

[0016] The concentration of the alkali fusibility resin in the photoresist application constituent of a quinone diazide system positive type is usually 1 - 30 % of the weight, and the concentration of a quinone diazide compound is usually 0.01 - 15 % of the weight. And it is usually twice [0.001 - 1.0 weight] the rate of the quinone diazide compound to an alkali fusibility resin of this. In the photoresist application constituent of a quinone diazide system positive type, additives, such as a sensitizer for the extinction nature material for lessening influence of the application nature improvement agent for raising application nature and the irregular reflection light from a substrate and the improvement in sensitivity, can be added.

[0017] The application constituent for the improvement in a performance in the lithography of this invention is used applying to the upper surface of the above quinone diazide system photoresist constituent application films. And although you may dissolve in any of an organic solvent or a water medium as long as it is alkaline, the viewpoint of an embodiment with desirable there being no mixing with the quinone diazide system photoresist constituent application film applied to the lower layer and a water developer developing negatives, dissolving and removing simultaneously with a photoresist application film, a bird clapper, etc. to a water-soluble application constituent is desirable.

[0018] The water which may contain the organic solvent which can be mixed with water, such as a methanol which may be replaced by the fluorine atom, ethanol, and an isopropanol, as a water medium is used. However, the amount of the organic solvent mixed from a viewpoint of mixing prevention has the fewer desirable one, and the amount of an organic solvent is 30

or less % of the weight usually 10 or less % of the weight still more preferably 20 or less % of the weight preferably as a rate over all media.

[0019] The application constituent of this invention usually contains film formation material. As this film formation material, from the same viewpoint as the above, a water-soluble thing is used suitably and water-soluble polymer, such as a polyacrylic acid, a polymethacrylic acid, polyvinyl alcohol, a polyvinyl pyrrolidone, a polyvinyl methyl ether, and a pullulan, is mentioned as a concrete film formation material. Such film formation material may substitute the after-mentioned water-soluble fluorine compound for a part or all. The amount of the film formation material used is usually 1 - 10 % of the weight preferably 0.1 to 20% of the weight to all application constituents. Since 1.5 or more things have many refractive indexes, the amount used has [such film formation material] the fewer desirable one. The method of substituting a fluorine compound for a part of film formation material is an embodiment desirable for the after-mentioned reduction in refraction. [0020] the alkaline strength of the application constituent of this invention -- pH of application constituent liquid -- carrying out -- usually -- 7.1-14 -- it is -- desirable -- 8-13 -- it is 8.5-12.5 still more preferably Alkalinity can be adjusted in organic amines, such as a tetramethylammonium hydroxide solution, etc.

[0021] The application constituent of this invention has an indispensable thing alkaline as mentioned above. By making it alkaline, a quinone diazide compound carries out the coupling reaction of the reason a good result is obtained to the alkali fusibility resin of a phenol nature compound under alkaline conditions, and the solubility over a developer is in a bird clapper small. And advance of the above-mentioned coupling reaction is influenced by conditions, such as alkaline intensity and ambient temperature.

[0022] Therefore, since optimum conditions change also with conditions of a photo lithography process, for example, baking, process, alkaline strength needs to take these into consideration synthetically, and needs to determine them. For example, it becomes difficult for the development remainder, such as scum, to occur, without the ability doing sufficiently greatly, after exposing the dissolution rate to the developer of an exposure portion, when alkali conditions are too strong also to remainder, and to attain the purpose of this invention, when alkali conditions are too weak also to remainder.

[0023] If a photosensitive acid generating compound is added to the application constituent of this invention, a still better result will be obtained. That is, although the development remainder, such as scum, may occur into an exposure portion in an alkali treatment as described above, since the alkali treatment also of the exposure portion it is not desirable carrying out an alkali treatment originally will be carried out, this is because the suitable width of face of process conditioning is narrow with the conventional technology. On the other hand, if a photosensitive acid generating compound is added to the application constituent of this invention, the exposure portion of an application constituent can be changed acid after exposure, consequently the alkali treatment of an exposure portion will be mitigated, and the development remainder, such as the above-mentioned scum, will be improved.

[0024] Although the compound containing the poly halogenated-hydrocarbon machine, an onium salt compound, a sulfonate compound, a sulfone compound, etc. are mentioned as a photosensitive acid generating compound, in these, the water-soluble thing which has a water fusibility machine in a molecule is used suitably.

[0025] As an example of a water-soluble photosensitive acid generating compound Diphenyliodonium hexafluorophosphonate, diphenyliodonium trifluoromethane sulfonate, Triphenyl sulfonium bromide, triphenyl sulfonium hexafluorophosphonate, Triphenylsulfonium trifluoromethane sulfonate, diphenyl-(4-methoxyphenyl) sulfonium trifluoromethane sulfonate, Tris (4-methoxyphenyl) sulfonium trifluoromethane sulfonate, Diphenyl-(4-(phenylthio) phenyl) sulfonium trifluoromethane sulfonate, Diphenyl-(4-(phenylthio) phenyl) sulfonium hexafluorophosphonate, Dimethyl-(4-hydroxy naphthyl) sulfonium trifluoromethane sulfonate, Onium salts, such as 2-naphtholmethyl tetramethylene sulfonium trifluoromethane sulfonate; sulfonic-acid amides, such as a benzenesulfonic-acid amide, a para-toluenesulfonic-acid amide, and benzenesulfonic-acid HIDORAJITO, are mentioned.

[0026] the mixing ratio of a photosensitive acid generating compound -- the mixing ratio to the component whole quantity excluding [the rate] the solvent of an application constituent -- as a rate -- usually -- 0.005 - 0.2 weight twice -- it is 0.01 - 0.1 weight twice preferably In addition, the addition of the aforementioned photosensitive acid generating compound also takes pH of application constituent liquid into consideration, is determined, and it is adjusted so that an exposure portion can be made acid after exposure.

[0027] Furthermore, the application constituent of this invention is made the composition which approaches [m0.5] when the refractive index to the incident-light wavelength of the application film expresses the refractive index of a lower layer photoresist constituent application film with [m]. And since influence of the aforementioned multiple echo in a film can be made small if the application thickness of the application constituent application film of this invention is increased $\lambda/4$ of odd times when incident-light wavelength is set to λ , it is desirable.

[0028] Since the refractive indexes of the usual photoresist constituent application film are usually 1.6-1.7, the desirable refractive index of the application film by the application constituent of this invention is set to 1.25-1.3. However, since it is very difficult to obtain this application film of a low refractive index in practice, realistic suitable ranges are 1.3-1.45. According to the application film of this refractive index, reflected light intensity becomes small by interferential action, and the size controllability to the application thickness of a photoresist constituent application film improves.

[0029] As a material for attaining the above-mentioned low refractive-index application film, a fluorine content compound is effective and it is desirable to add a water-soluble fluorine content compound to the application constituent of this invention. In the below-mentioned water-soluble fluorine compound and/or one atmospheric pressure of 20 degrees C which are a solid-state, it is liquefied, and the below-mentioned water-soluble fluorine compound whose boiling point in one atmospheric

pressure is 100 degrees C or more is mentioned in the water-soluble fluorine compound of 20 degrees C indicated as a desirable water-soluble fluorine content compound by the Japanese-Patent-Application-No. No. 64132 [seven to] specification already submitted by these people, i.e., one atmospheric pressure. Especially, by use of such mixture, the amount of the film formation material used, such as the aforementioned polyacrylic acid, can be lessened, and, moreover, the 1.45 or less aforementioned application film of a low refractive index can be obtained. The amount of the fluorine content compound used is usually 1 - 10 % of the weight preferably 0.1 to 20% of the weight to all application constituents like film formation material.

[0030] As a water-soluble fluorine compound which is a solid-state, in one atmospheric pressure of 25 degrees C, it is the water-soluble fluorine compound which is a solid-state, and 150 degrees C or more of 200 degrees C or more of boiling points of one atmospheric pressure are a compound 250 degrees C or more still more preferably in the one above-mentioned atmospheric pressure of 20 degrees C preferably. Water solubility usually means dissolving 1% of the weight or more preferably 0.1% of the weight or more to the aforementioned aqueous medium under a 20-degree C condition here under 1 atmospheric pressure.

[0031] as the above-mentioned water-soluble fluorine compound -- a carbon number -- usually -- 3-30 -- the perfluoro alkyl sulfonic acid and perfluoroalkyl carboxylic acid of 5-20 are mentioned preferably as other examples -- a carbon number -- usually -- 8-40 -- the perfluoroalkyl benzenesulfonic acid of 9-20, a perfluoro alkyloxy benzenesulfonic acid, a perfluoroalkyl benzene carboxylic acid, and a perfluoroalkyl oxybenzene carboxylic acid are mentioned preferably furthermore -- as other examples -- a carbon number -- usually -- 4-1000 -- the perfluoroalkyl polyether sulfonic acid and perfluoroalkyl polyether carboxylic acid of 4-500 are mentioned preferably It is used as a free acid, and also these fluorine content acid compounds are used with forms, such as an ammonium salt, and monochrome which may be replaced with the fluorine - tetra-alkyl ammonium salt, and may be used as two or more kinds of mixture.

[0032] As an example of the above-mentioned fluorine content acid compound A perfluoro butane sulfonic acid, a perfluoro heptane sulfonic acid, A perfluoro octane sulfonic acid, a perfluoro decane sulfonic acid, A perfluoro butanoic acid, a perfluoro adipic acid, a perfluoro octanoic acid, Perfluoroazelaic acid, perfluoro sebacic acid, perfluoro -1, 10-Decan dicarboxylic acid, Perfluoro heptaoxy benzene sulfonic acid, a perfluoro (2-ethoxy ethane) sulfonic acid, A perfluoroalkyl polyether sulfonic acid (for example, goods made from E.I.duPont "Nafion"), Perfluoro -2, the 5-dimethyl -3, 6-dioxo nonoic acid, perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoic acid, a perfluoroalkyl polyether dicarboxylic acid, etc. are mentioned. Moreover, as an example of the water-soluble fluorine compound of other solid-states, fluoro alkyl alcohols, such as the 2, 2, 3, 3, 4, and 4-hexafluoro pentane -1, 5-diol, 2, 2, 3, 3, 4, 4 and 5, 5-OKUTA fluoro hexane -1, and 6-diol, and the fluorochemical surfactant by MITSUBISHI MATERIALS CORP., "EF-121" (tradename) etc., are mentioned. [for example,]

[0033] On the other hand, in the one aforementioned atmospheric pressure of 20 degrees C, it is liquefied, and is preferably liquefied in one atmospheric pressure of 10 degrees C as a water-soluble fluorine compound whose boiling point in one atmospheric pressure is 100 degrees C or more, and 100 degrees C or more of 150 degrees C or more of boiling points in one atmospheric pressure are a water-soluble fluorine compound 200 degrees C or more more preferably still more preferably. Water solubility usually means dissolving 1% of the weight or more preferably 0.1% of the weight or more to the aforementioned aqueous medium under a 20-degree C condition here under 1 atmospheric pressure.

[0034] As the above-mentioned water-soluble fluorine compound, although an acid compound like a trifluoromethane sulfonic acid and a heptafluoro butanoic acid can also be used for example, in order to suppress the corrosion of a device etc., as for these acid compounds, avoiding is desirable [using it so much]. From this viewpoint, a neutral compound is desirable as the above-mentioned water-soluble fluorine compound. The compound expressed in the following chemical formula as a neutral water-soluble fluorine compound is mentioned.

[0035]

[Formula 1]

$R1-(R2-O)m-(CX2)_n-CX(OH)-CX2(OH)$

[0036] the inside of the above-mentioned chemical formula, and R1 A fluorine content alkyl group and R2 the alkylene machine which may contain a fluorine is expressed, X expresses a hydrogen atom or a fluorine atom, and these are the same -- or you may differ m and n express the integer of 0-5.

[0037] As an example of a neutral water-soluble fluorine compound expressed with the above-mentioned chemical formula, it is 3-(2-perfluoro hexyl) ethoxy. - Since ablation of the pattern imprinted after exposure/development etc. is caused, the perfluoroalkyl alcoholic ethylene oxide addition product or its end alkyl ether compound like [although 1 and 2-dihydroxy propane etc. is mentioned] the alpha-perfluoro NONENIRU-omega-methoxy polyoxyethylene which is an analogous compound are not desirable.

[0038] As other neutral water-soluble fluorine compounds, fluoro alkyl alcohols, such as 2, 2, 3, and 3-tetrafluoro propanol, 2, 2, 3, 3 and 4, a 4-hexafluoro butanol, 2, 2, 3, 3, 4, 4 and 5, and 5-OKUTA fluoro pentanol, the Sumitomo 3M fluorochemical surfactant "FC-171" (perfluoroalkyl alkoxylate), for example, goods, "FC-430" (fluoridation alkyl ester), etc. are mentioned.

[0039] The above-mentioned fluorine compound is used as two kinds or more besides independent use of mixture, and the boiling point of one atmospheric pressure gives a result especially with the desirable use as mixture of a compound [200 degrees C / or less] 100 degrees C / or more / and a compound 200 degrees C or more.

[0040] The fluorine substitution rate has the desirable higher one, and the water-soluble fluorine compound of the

aforementioned solid-state or a liquid is usually 70% or more preferably 50%, although the hydrogen atom of an alkyl group is the compound replaced by the fluorine atom.

[0041] A water-soluble fluorine compound is added and used for the aforementioned film formation material. and -- although one kind is sufficient as the addition -- solid fluorine compounds and the fluorine compounds of a liquid -- a weight rate -- usually -- 10:1- by 5:1-1:10 being comparatively alike preferably 1:20, and carrying out mixed use, even if there is no use of film formation material, the application film of a low refractive index can be formed good

[0042] Moreover, if the application constituent of this invention is made to contain the compound to which the absorbance of the application film to the wavelength of an incident light decreases by projection of the incident light concerned, the contrast of the light of the exposure section within a photoresist application film and the unexposed section will improve, a high definition will be obtained, and it will be desirable at **. the reduction rate of an absorbance -- the reduction before and behind full change -- comparatively -- carrying out -- usually -- it is 50% or more still more preferably 30% or more preferably 10% or more

[0043] As the above-mentioned compound for absorbance reduction, an alpha-carboxy-N-methyl nitron, An alpha-(p-(dimethylamino) phenyl)-N-(4-carboxyphenyl) nitron, An alpha-(p-(diethylamino) phenyl)-N-(4-carboxyphenyl) nitron, An alpha-(p-(dimethylamino) phenyl)-N-(2-methyl-4-carboxyphenyl) nitron, An alpha-(p-(diethylamino) phenyl)-N-(2-methyl-4-carboxyphenyl) nitron, An alpha-(p-(dimethylamino) styryl)-N-(4-carboxyphenyl) nitron, An alpha-(p-(diethylamino) styryl)-N-(4-carboxyphenyl) nitron, An alpha-(p-(dimethylamino) styryl)-N-(2-methyl-4-carboxyphenyl) nitron, an alpha-(p-(diethylamino) styryl)-N-(2-methyl-4-carboxyphenyl) nitron, etc. are mentioned.

[0044] the mixing ratio of the compound for absorbance reduction -- as the rate over the component whole quantity excluding [the rate] the solvent of an application constituent -- usually -- 0.01 - 0.5 weight twice -- it is 0.1 - 0.4 weight twice preferably

[0045] Fundamentally as the pattern formation method which used the application film by the application constituent of this invention, the same method as the case of the usual quinone diazide system positive-type photoresist which forms application films, such as a protective coat, in the photoresist application film upper surface is employable. Specifically, the following procedure is employable.

[0046] First, after applying a quinone diazide system positive-type photoresist constituent to a substrate, the solvent which prebakes and (1) remains is evaporated. Subsequently, after applying the application constituent of this invention on a quinone diazide system positive-type photoresist constituent application film, the solvent which prebakes and (2) remains is evaporated. In addition, prebaking (1) can be omitted, and the solvent of the application film of each step can also be simultaneously evaporated in prebaking (2), and prebaking (2) can also be omitted.

[0047] Subsequently, it exposes and a pattern latent image is made to form. g line, i line, excimer laser light, etc. can perform exposure, and the application constituent of this invention can respond to all such exposure wavelength. Of course, optimization of the material to exposure wavelength etc. is performed. Subsequently, BEKU is performed after exposure, and negatives are developed, and a pattern is made to form. As a developer, usually, organic amine solution is used and the solution of a tetramethylammonium hydroxide and/or a choline is used suitably. Moreover, after dissolving with water and removing the application film by the application constituent of this invention in advance of contact to a developer, you may contact a quinone diazide system positive-type photoresist application film and a developer.

[0048]

[Example] Hereafter, although an example explains this invention still in detail, this invention is not limited to the following examples at all, unless the summary is exceeded.

[0049] ((A) The example of surface application constituent manufacture) 3.6g of salts, 3-(2-trideca fluoro hexyl) ethoxy which neutralized the heptadeca fluoro octane sulfonic acid in tetramethylammonium hydroxide (100% of neutralization indices) - 1 and 2-dihydroxy propane 2.4g and 2-naphtoilmethyl tetramethylene sulfonium trifluoromethane sulfonate 0.6g were dissolved in 96g of water. Furthermore, pH of a constituent solution was adjusted to 10 in tetramethylammonium hydroxide. This solution was filtered with the 0.2-micrometer filter, and the surface application constituent A was prepared.

[0050] ((B) The example of surface application constituent manufacture) In the example A of surface application constituent manufacture, the surface application constituent B was prepared like the example A of surface application constituent manufacture except not using 2-naphtoilmethyl tetramethylene sulfonium trifluoromethane sulfonate.

[0051] ((C) The example of surface application constituent manufacture) In the example A of surface application constituent manufacture, the surface application constituent C was prepared like the example A of surface application constituent manufacture except having changed the neutralization index in tetramethylammonium hydroxide to 95%, and having changed pH of a constituent solution into 3.5.

[0052] 2.0g of salts which neutralized the heptadeca fluoro octane sulfonic acid in tetramethylammonium hydroxide (100% of neutralization indices), ((D) The example of surface application constituent manufacture) 3-(2-trideca fluoro hexyl) ethoxy - 1, 2-dihydroxy propane 4.0g, 2-naphtoilmethyl tetramethylene sulfonium trifluoromethane sulfonate 0.7g, alpha-[p-(dimethylamino) phenyl]-N-(4-carboxyphenyl) nitron 2.0g is added to 91g of water, and pH of a constituent solution is further adjusted to 10 in tetramethylammonium hydroxide. It was made to dissolve. This solution was filtered with the 0.2-micrometer filter, and the surface application constituent D was prepared.

[0053] The spin coat of examples 1-2 and the example 1 of comparison - the quinone diazide system positive-type photoresist (tradename : MCPRI6600) by 2 Mitsubishi Chemical was carried out to the 5 inches silicon wafer of four sheets, respectively,

further, surface application constituent A-C was applied to the silicon wafer of three sheets in it, respectively, heating BEKU was carried out for 60 seconds at 70 degrees C on the hot plate, and the application film was dried (examples 1-2 and example 1 of comparison). The application thickness of about 1 micrometer and a surface application constituent of the application thickness of a photoresist was about 670A.

[0054] Subsequently, it exposed by i line stepper (tradename : NSR1755i7A) by NIKON CORP., and, and further, after carrying out rinse removal of the surface application constituent with water, paddle development was carried out for 60 seconds in 2.38% of the weight of tetramethylammonium hydroxide solution. [on the hot plate] [120 degrees C] [for 90 seconds] [after exposure] 0.5-micrometer L&S (ratio of line breadth and space width of face) observed the pattern configuration etc. with the light exposure finished in 1:1. Exposure development was performed without applying a surface application constituent about one in the silicon wafer of four sheets (example 2 of comparison).

[0055] Consequently, in the case of the example 1 which performed exposure development using the surface application constituent A, it is [it is resolving with sufficient rectangle nature to 0.34 micrometers, and / no scum] and was good. Moreover, although the rectangle nature of a pattern was well resolved to 0.35 micrometers in the case of the example 2 which performed exposure development using the surface application constituent B, scum was generated a little. On the other hand, in the case of the example 1 of comparison which performed exposure development using the surface application constituent C, it resolved only to 0.36 micrometers, but it was inferior to the case of an example 1 also in rectangle nature. Moreover, although resolved to 0.36 micrometers in the case of the example 2 of comparison which performed exposure development, without using a surface application constituent, rectangle nature was inferior to the case of an example 1.

[0056] Moreover, when the depth of focus was measured, the case where the surface application constituent A is used was the largest, and when the surface application constituent B is used, the case where a surface application constituent is not used is an abbreviation EQC, and it was inferior to the case where the surface application constituent A is used.

[0057] The application film was formed so that an example 3 and the quinone diazide system positive-type photoresist (tradename : MCPRI6600) by example of comparison 3 Mitsubishi Chemical, and the surface application constituent A are used, and each operation of BEKU might be performed to two or more wafers from an application like an example 1, it might become the range of 10000-12000A at the interval whose photoresist application thickness is about 100A and the application thickness of the surface application constituent A might become 670A (example 3). Moreover, the wafer in which the photoresist application film was formed was prepared like the above for comparison except not applying a surface application constituent (example 3 of comparison).

[0058] Subsequently, each operation of development was performed from exposure like the example 1. The result line width of the 0.5-micrometer mask pattern image in the same light exposure was measured with the electron microscope.

Consequently, the change of a result line width to thickness change of a photoresist application film was good to ** as compared with the example 3 of comparison which performed exposure development, without the direction of the example 3 which performed exposure development using the surface application constituent A using a surface application constituent.

[0059] The example 4 and the quinone diazide system positive-type photoresist (tradename : MCPRI6600) by example of comparison 4 Mitsubishi Chemical, and the surface application constituent D were used, and each operation of development was performed from exposure like the example 1 except having made the application thickness of the surface application constituent D become 640A (example 4). Moreover, the wafer which formed the photoresist application film similarly was prepared for comparison except not applying a surface application constituent (example 4 of comparison). The dependency of resolution, the rectangle nature of a pattern, the depth of focus, and the pattern size to photoresist application thickness was good as compared with the example 4 of comparison which performed exposure development, without the direction of the example 4 which performed exposure development using the surface application constituent D using a surface application constituent altogether.

[0060]

[Effect of the Invention] According to this invention explained above, by the easy method of applying one kind of surface application constituent, the configuration and the depth of focus of an imprint pattern are good, and change by the application thickness of an imprint pattern size is small, and can form the pattern of a good result by high resolving.

[Translation done.]